The Effect of Polar Soil Components on the Phase Inversion Temperature and Optimum Detergency Conditions

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Previously reported results have shown that optimum removal of a hydrocarbon soil from polyester/cotton fabric occurs above the cloud point at the phase inversion temperature (PIT) of nonionic surfactant/water/soil systems. Through comparison of phase behavior measurements to radiotracer detergency studies using model sebum soils, i.e., cetane/oleyl alcohol and cetane/oleic acid blends, the relevance of the PIT for removal of nonpolar/polar soil mixtures has also been demonstrated. For these soils, the PIT is typically below the cloud point, and the highest level of soil removal is found between the PIT and cloud point rather than only at the PIT. This relatively temperature-insensitive soil removal is attributed to the preferential solubilization of polar soil components which continually changes the composition of the residual soil during the washing cycle. These findings explain the long-observed results that 4- to 5-EO alcohol ethoxylates are preferred for the removal of nonpolar soils while 6- to 9-EO ethoxylates are the more effective surfactants for sebum soils.

KEY WORDS: **Detergency, inversion, optimum, phase, polar, soil, temperature.**

Nonionic surfactants, such as alcohol ethoxylates, have long been regarded as being very effective for the removal of nonpolar soils, such as mineral oil, from polyester/cotton fabric blends. This effectiveness can be maintained even at low washing temperatures where soil removal for that particular soil-fabric combination is most difficult. Specifically, previous work using a radiotracer detergency technique has shown that a high level of detergent activity can be achieved in cold water through adjustment of a surfactant system's solubility, i.e., its cloud point, by addition of various hydrophobic additives such as long- chain alcohols (1,2).

Detailed study of model soil and surfactant systems has shown that optimum mineral oil removal is, in fact, achieved at the phase inversion temperature (PIT) where the interfacial tension between soil and water is lowest and the soil-solubilization rate and capacity are highest (3-5). Also, at the PIT with soils such as cetane (hexadecane) or 1:1 blends of cetane and squalane, alcohol ethoxylates are well above their cloud point and in the liquid crystal regime (4,6). Microscopic observation of the dynamic phenomena accompanying contact of liquid crystal phases with hydrocarbon has indicated that these structures solubilize large quantities of oil and also promote the formation of oil-rich microemulsion phases (7). This finding of enhanced detergent activity at the PIT contradicts the conclusion of some studies that washing above the cloud point is generally undesirable (8,9).

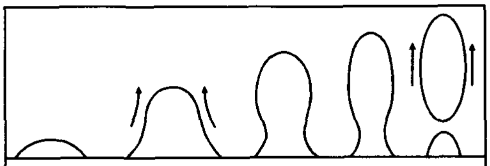
However, many commonly encountered soils, such as sebaceous soils, are not strictly nonpolar but also contain surface-active long-chain alcohols and acids. For example, Table 1 shows the composition of a synthetic sebum soil developed for radiotracer detergency testing (1,10). The optimal removal conditions for these complex soil mixtures are generally quite different than for nonpolar soils. As a result, at the same washing temperature, the optimum nonionic surfactant for removing sebum from synthetic fabrics is significantly more water-soluble than the optimum surfactant for mineral oil or triglyceride removal (11-13).

TABLE 1

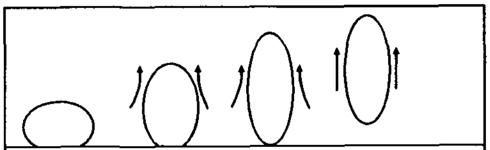
Composition of Synthetic Sebum

Component	Concentration (wt%)
Mineral oil	25
Triglycerides	30
Fatty acids	30
Fatty alcohols	15

Because of the importance and prevalence of liquid nonpolar/polar soil blends in many practical situations, knowledge of the mechanisms by which they are removed from fabrics would be of great utility to the detergent industry. Past work has focused on observing how model nonpolar/polar soil mixtures are removed from flat films of polyester (14,15) or from single threads (16). In general, the presence of polar components in very small quantities was found to increase the rate of emulsification of the soil into the aqueous nonionic surfactant solution. The observed mechanism was similar to that shown in Figure 1a, where the soil-substrate contact angle is found to remain low while a reduction in soil-water interfacial tension allows snap-off of droplets from the top layer of soil (17). This sequence of events contrasts with that of conventional roll-up (Fig. 1b), where water preferentially wets the fabric substrate, thereby removing the entire liquid soil drop in one step.



(a) Emulsification Resulting from Soil – Water Interfacial Tension Reduction



(b) Roll – Up Resulting from Fabric Wetting

FIG. 1. Mechanisms of liquid soil removal (adapted from reference 17).

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In this paper, a comprehensive study of model mixed soil systems is reported in which detergency tests are interpreted by the results of various physical property measurements using the same soil/water/surfactant systems. The properties investigated include phase inversion temperatures, interfacial tensions and soil solubilization rates. Also, soil release from polyester substrates was observed microscopically. In addition to providing insight into the relevant detergency mechanisms, these tests were performed with the hope of finding new techniques by which nonionic surfactants can be evaluated for their efficacy against nonpolar/polar soil mixtures.

EXPERIMENTAL PROCEDURES

Phase inversion temperature (PIT) measurements were made based on the emulsion stability of equal weight mixtures of oil and 5% aqueous surfactant solution (18). While periodically being shaken by hand, the samples were observed at increasing temperatures in a thermostatically-controlled water bath. The temperature at which the most rapid separation into three phases (excess water, excess oil and a middle microemulsion phase) occurred was taken to be the PIT.

The solubilization studies were performed using an *in situ* turbidity technique (1). Small volume soil samples were injected by syringe into a detergent solution stirred by a Kraft Model S-70 nonaerating stirrer (Kraft Apparatus, Inc., New York, NY). Solubilization rates were determined by monitoring electrical outputs of solution turbidity using a Brinkmann PC800 dipping probe colorimeter (Brinkmann Instruments Ltd., Toronto, Canada). In this study, four separate 10-μL injections of soil were made into 100 mL of 0.1% surfactant solution to obtain an average value. Because the degree of turbidity initially generated by the soil addition differed greatly among the soil samples, comparison of solubilization rates was not made based on the rate of turbidity decrease from its maximum value but rather on the elapsed time between initial injection and complete solubilization.

Interfacial tensions were measured at 25°C using a University of Texas Model 500 spinning drop tensiometer. Details of this technique, which is the most suitable for systems exhibiting very low interfacial tensions, may be found elsewhere (19). A 3-μL oil drop was injected into the sample tube outside of the apparatus, the tube was then quickly placed in the tensiometer and spinning was initiated. The elapsed time of an experiment was measured from drop injection.

Microscopic soil-release studies were performed using a Ramé-Hart Model 100 goniometer equipped with a Model 100-07 environmental chamber (Ramé-Hart, Inc., Mountain Lakes, NJ). Soil removal processes were recorded with a JVC BY-100 video camera. Various polyester substrates were studied, including fibers, mesh and film. A 1-μL oil drop was applied by syringe to the clean substrate which was held by clamps within the environmental chamber. Twenty mL of detergent solution was then carefully injected into the rectangular quartz cell surrounding the mounted substrate. The temperature of the sample was controlled by a circulating water bath, and moderate agitation was supplied by a small propeller stirrer (Instech Laboratories, Horsham, PA) which was placed through the top of the environmental chamber.

Terg-o-tometer detergency tests were performed using a standard radiolabeled soils detergency procedure (1,20). Surfactants and soils which were studied are shown in Table 2. The oleyl alcohol (*cis*-9-octadecen-1-ol) and oleic acid (*cis*-9-octadecenoic acid) were obtained from Sigma Chemical Co. (St. Louis, MO) and had a stated purity of 99%. For the terg-o-tometer experiments, the cetane and oleic acid were labeled with tritium-tagged and ^{14}C- tagged compounds, respectively. A radioactive label was not used with oleyl alcohol.

TABLE 2

Surfactants, Soils and Fabric Used in Radiotracer Detergency Studies

Surfactants	Soils[a]
$C_{12}E_5$	Cetane
$C_{12}E_6$	9:1 Cetane/oleyl alcohol
$C_{12}E_7$	3:1 Cetane/oleyl alcohol
$C_{12}E_8$	1:1 Cetane/oleyl alcohol
N25-9[b]	9:1 Cetane/oleic acid
	3:1 Cetane/oleic acid

[a] Cetane, ^{3}H-labeled; Oleic Acid, ^{14}C-labeled; Oleyl Alcohol, Unlabeled.
[b] Commercial alcohol ethoxylate containing 9 EO groups.
Fabric was 65:35 permanent press polyester/cotton.

The specific (i.e., single-component) alcohol ethoxylates based on n-dodecanol were obtained from Nikko Chemical Company (Tokyo, Japan) and used as received. A commercial broad-distribution ethoxylate having a C_{12}-C_{15} hydrophobe of high linearity and an average of nine ethylene oxide units, denoted here as N25-9, was obtained from Shell Chemical Company (Houston, TX).

Soil removal was measured from one 65:35 polyester/cotton fabric swatch initially containing 28 mg of soil. This loading corresponds to a soil-to-fabric weight ratio of 0.025. Absolute soil removal levels were obtained by liquid scintillation counting of radioactivity in the wash water. Also, the surfactant concentration was kept constant at 0.05% wt.

No water hardness was used to simplify comparison of the detergency results to phase behavior measurements. In the detergency study with 3:1 cetane/oleyl alcohol soil, 1 mL of 2.5% triethanolamine (TEA) was used to increase the pH of the washing solution to 7-8. However, no TEA was used in the presence of the oleic acid soils to prevent neutralization of the acid into its oleate form. The washing time was 10 min for all experiments except those investigating the kinetics of soil removal. The reported results are all averages of duplicate runs.

RESULTS

Polar soil effects on the phase inversion temperature. Figure 2 contains plots of PIT vs overall oil composition for specific ethoxylates using the cetane/oleyl alcohol blends at a constant weight ratio of surfactant to oil of 0.05. Although the PIT of these systems shows some dependence on this ratio due to unequal partitioning of the oil components (21), the effect was found not to be significant if at least a 10:1 ratio of oil to surfactant was present.

As shown in Figure 2, the presence of rather small quantities of oleyl alcohol has a dramatic effect on the PIT. In fact, only about 3% polar material is sufficient to lower the PIT to

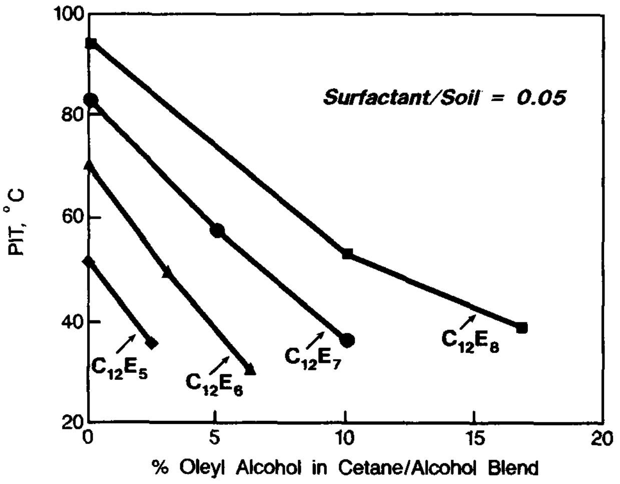


FIG. 2. PIT vs oleyl alcohol content in cetane/alcohol blend.

the cloud point temperature. This large effect results from the alcohol behaving as a low-HLB (hydrophile-lipophile balance) emulsifier which interacts with the high-HLB surfactant at the oil-water interface and lowers the PIT. Not surprisingly, therefore, the higher-HLB surfactants, e.g., $C_{12}E_8$, required more polar oil to attain a given PIT than less hydrophilic surfactants such as $C_{12}E_5$.

Nearly identical PIT-composition plots were found using oleic acid as the polar additive as shown in Figure 3. These results indicate that, at the pH conditions studied (pH 5 to 6), the oleic acid was ionized to a very limited extent. Any formation of water- soluble oleate ions would be expected to counteract the lowering of the PIT. The similar results found for oleyl alcohol and oleic acid are consistent with previous studies examining the effect of the addition of a variety of long-chain acids and alcohols on the PIT of a commercial nonionic surfactant-paraffin oil system (22).

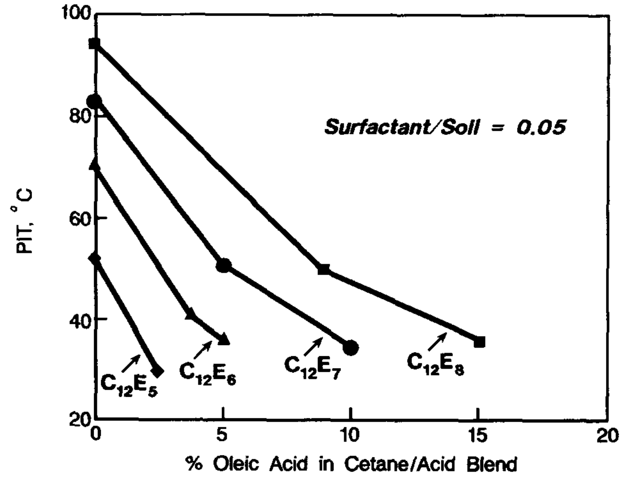


FIG. 3. PIT vs oleic acid content in cetane/acid blend.

Interfacial tension and solubilization rate studies. Figure 4 shows dynamic interfacial tension (IFT) measurements for cetane/oleyl alcohol blends in the same composition range as those used in the PIT measurements. The weight ratio of oil to surfactant in these studies was kept constant at 10. A strong dependence on oil composition is seen with the highest interfacial tensions exhibited by the systems having the highest oleyl alcohol content. For the 10 and 15% alcohol cases, a dramatic decrease in IFT to values below 0.1 dyne/cm occurred several minutes into the experiments. Not surprisingly, the composition yielding the lowest equilibrium IFT (15% alcohol) corresponded closely to the composition yielding a PIT of 25°C with $C_{12}E_7$. With no oleyl alcohol present, the equilibrium IFT is two orders of magnitude higher than this optimum case.

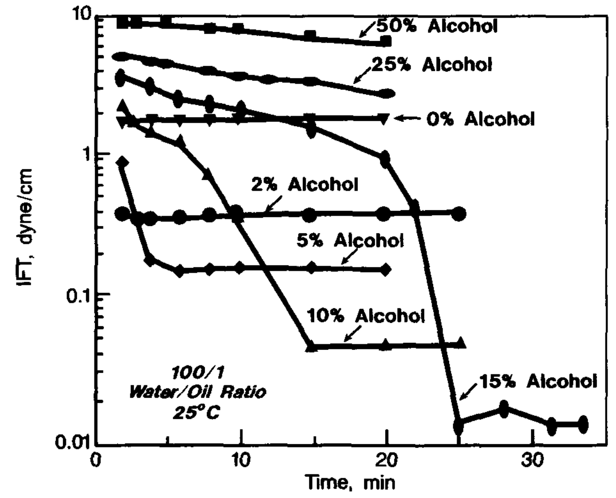


FIG. 4. IFT's of 0.1% $C_{12}E_7$ with cetane/oleyl alcohol blends.

The effect of varying the EO-chain length of the surfactant is shown in Figure 5. For the 10% alcohol oil, the lowest equilibrium IFT was obtained with $C_{12}E_6$. This result correlates well with the data in Figure 2, which indicates that the amount of polar alcohol in that oil is only slightly higher than that yielding a PIT of 25°C with $C_{12}E_6$. Although these experiments indicated that the time required for the attainment of ultralow IFTs is longer than normal washing cycles, much shorter times undoubtedly would be required to attain the same low IFTs at the surfaces of very thin liquid soil films present in unwashed fabric.

Figure 6 contains plots of the average solubilization rates at

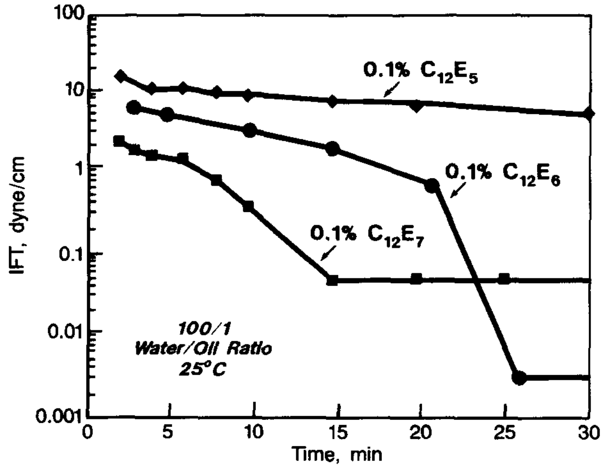


FIG. 5. Effect of surfactant structure on IFT's with a 90:10 cetane/oleyl alcohol blend.

55°C of various cetane/oleyl alcohol and cetane/oleic acid blends into 0.1% $C_{12}E_7$. The final soil-to-surfactant ratio in these studies was nearly identical to that present in the detergency experiments. A clear maximum is observed in each curve at a specific polar soil content. Also, as would be expected based on the PIT studies, the oleyl alcohol and oleic acid behaved very similarly at these low-pH conditions in terms of the magnitude of the rates and at what concentration the maximum rate (minimum solubilization time) occurs at each temperature.

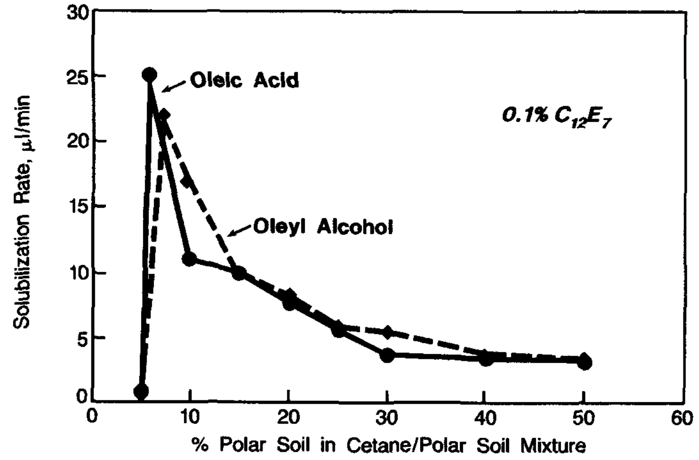


FIG. 6. Average solubilization rate at 55°C vs soil composition.

Similar behavior was exhibited by the other surfactants studied. Table 3 summarizes the results for the oleyl alcohol soils and shows that the concentration ranges where the highest solubilization rates were found correspond closely to the compositions exhibiting phase inversion as interpolated from the data in Figure 2. The oleic acid soils exhibited the same correlation between PIT and fast soil-solubilization rates. As a consequence of this relationship, the more water-soluble surfactants require large amounts of polar material to achieve high rates at low temperatures. For example, the multicomponent N25-9 and the specific $C_{12}E_8$, which each have a cloud point around 80°C, require approximately 30% oleyl alcohol to achieve high soil-solubilization rates at 25°C.

TABLE 3

Weight% Oleyl Alcohol in Cetane/Alcohol Blend Yielding Maximum Rate of Oil Solubilization

Surfactant[a]	25°C	45°C	55°C
$C_{12}E_5$	4-6(4)[b]	–	–
$C_{12}E_6$	6-8(7)	4-6(4)	–
$C_{12}E_7$	15-17.5(13)	–	6-8(6)
$C_{12}E_8$	30-35(25)	–	10-12(10)
N25-9	30-35	–	10-15

[a] 0.1% in deionized water.

[b] Approximate concentration at PIT shown in parentheses.

In summary, very good agreement is found between those soil compositions yielding the highest solubilization rate at a particular temperature and those exhibiting phase inversion at the same temperature. Apparently, the low interfacial tensions which occur near the PIT allow very small oil drops to form which are quickly solubilized into the surfactant solution. Therefore, solubilization rate studies appear to be an excellent alternative method for determining regimes of low interfacial tension for both single-component and commercial surfactant systems. This conclusion is valid only for nonpolar/polar soil blends, however, since the phase inversion temperatures for strictly nonpolar soils typically are above the cloud point, making solubilization rate studies in the low-IFT temperature regime impossible by the turbidity technique.

Detergency studies. In agreement with previous results for cetane soil removal by specific alcohol ethoxylates (3,4), high levels of soil removal occurred at the PITs of the cetane/water/surfactant systems as shown in Table 4. In the cases of $C_{12}E_5$, $C_{12}E_6$ and $C_{12}E_7$, these temperatures are 50, 70 and 85°C, respectively. Only in the vicinity of these temperatures, which are 15-20°C above the respective surfactant solution cloud point, are ultralow interfacial tensions ($<10^{-2}$ dyne/cm) attainable.

TABLE 4

Optimum Detergency Temperatures for Removal of Cetane and 9:1 Cetane/Oleyl Alcohol Soils

		Opt. det. temp.	
Surfactant	Cloud pt.	Cetane	9:1 Cetane/alcohol
$C_{12}E_5$	35°C	50°C	20-30°C
$C_{12}E_6$	53°C	70°C	20-50°C
$C_{12}E_7$	68°C	85°C	40-60°C
$C_{12}E_8$	80°C	95°C	50-70°C

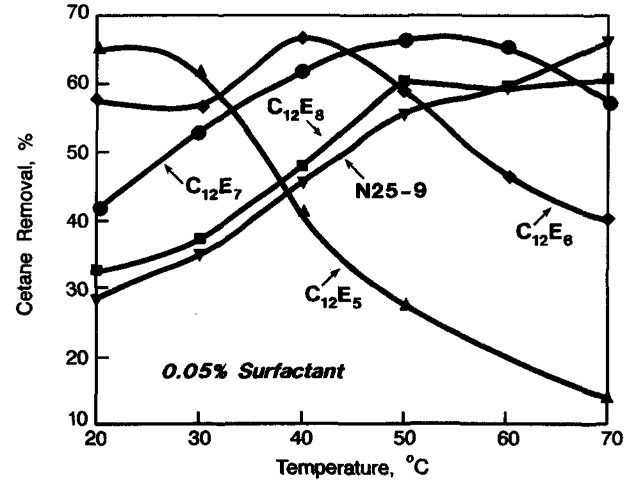


FIG. 7. Cetane removal from 9:1 cetane/oleyl alcohol soil.

Shown in Figure 7 are plots of cetane removal from the 9:1 cetane/alcohol soil vs wash temperature for five surfactant systems. Several interesting trends are apparent. At 20°C, detergency was found to increase with decreasing ethylene oxide content, while the reverse was true at 70°C. Also, optimum detergency was observed in the temperature intervals listed in Table 4. Not unexpectedly, based on the PIT results shown in Figure 2, optimum detergency occurred at lower wash temperatures for the mixed soil as compared to the cetane-only soil. In fact, optimum detergent activity was found below the surfactant cloud point for this slightly polar soil blend, with much lower soil removal occurring at higher temperatures. Very similar detergency-temperature profiles were found for N25-9 and $C_{12}E_8$, indicating that the effect of ethylene oxide distribution on cleaning performance is quite small for this soil-fabric combination.

Figure 8 shows the detergency-temperature profiles for the 3:1 cetane/oleyl alcohol soil. For $C_{12}E_7$, very high cetane removal was observed over the entire temperature range from 20 to 70°C. This insensitivity to wash temperature is in sharp contrast to the temperature sensitivity characteristic of nonpolar soil removal by alcohol ethoxylates. At the lower temperatures, $C_{12}E_5$ and $C_{12}E_6$ were not quite as effective as $C_{12}E_7$, but still gave quite high levels of soil removal. At increasing temperatures, however, the $C_{12}E_5$ and $C_{12}E_6$ systems exhibited a sharp drop-off in detergency. As found with the 9:1 soils, these changes occurred at temperatures quite close to the cloud points for the surfactants. A similar drop-off would probably have been observed with $C_{12}E_7$ if higher temperatures had been studied.

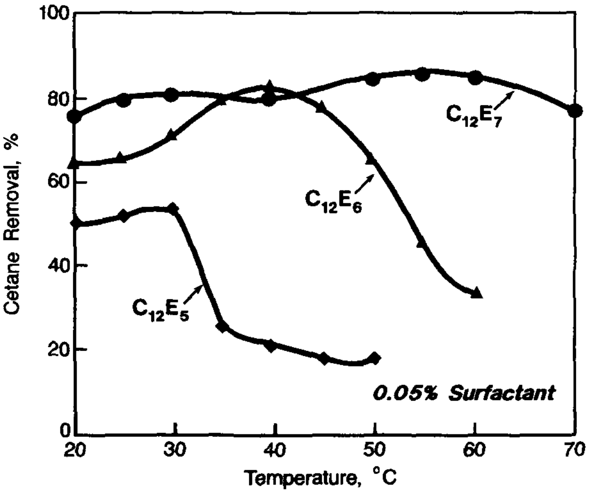


FIG. 8. Cetane removal from 3:1 cetane/oleyl alcohol soil.

Just as found in the PIT and solubilization studies, quite similar trends were obtained in the detergency studies when oleic acid was substituted for oleyl alcohol. The results for a 3:1 cetane/oleic acid soil are given in Figure 9. Interestingly, the data show that the removal of ^{14}C-labeled oleic acid parallelled that of cetane, although at 10-20% higher levels, indicating that preferential solubilization of oleic acid was occurring. Presumably, similar data would have been found for the soils containing oleyl alcohol if the alcohol had been radioactively tagged.

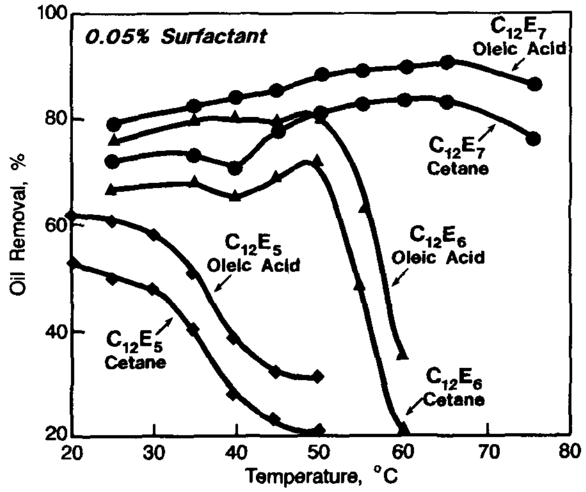


FIG. 9. Oil removal from 3:1 cetane/oleic acid soil.

DISCUSSION

Proposed mechanism of soil removal. The detergency data shown in Table 4 and Figures 7 and 8 indicate that, for a given surfactant, a minimum quantity of polar material in the soil is necessary to attain high soil removal at the washing temperature. Or, looked at in the opposite manner, a minimum temperature is required for optimized removal of a given soil mixture. This minimum temperature is the PIT as read off the curves in Figures 2 and 3. For example, 10% oleyl alcohol is sufficient to lower the PIT with $C_{12}E_6$ down to about 20°C, thereby greatly increasing soil removal at that temperature. In contrast, one must wash at 50°C to attain comparable removal of the same soil with $C_{12}E_8$. In general, the correlation of PIT with detergency explains why water-soluble ethoxylates, e.g., detergent-range alcohols with 6- to 9-EO, are the more effective detergents for sebum-like soils. These nonionics are the surfactants having PIT values falling in the normal temperature range for household laundry processes.

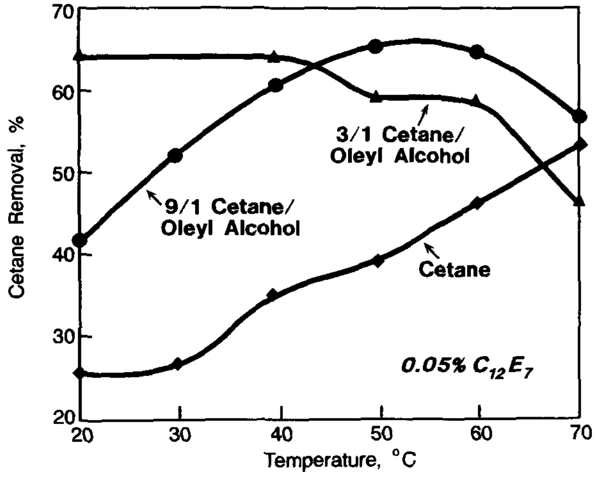


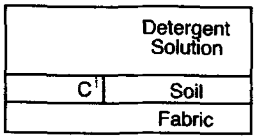
FIG. 10. Effect of oleyl alcohol content on cetane removal.

To further illustrate the correlation of detergency with phase behavior, Figure 10 shows the results of a detergency study investigating the effect of soil polarity on cetane removal by 0.05% $C_{12}E_7$ in the absence of triethanolamine. While detergency peaks near 80°C with cetane soil, good detergency is obtained at much lower temperatures with the polar soils. In agreement with the PIT data in Figure 2, maximum detergency is reached near 40°C with 10% oleyl alcohol in the soil while high levels of cetane removal are attained even at 20°C with 25% oleyl alcohol present. A similar interpretation of the detergency data for the other surfactants can be made using the PIT-soil composition plots.

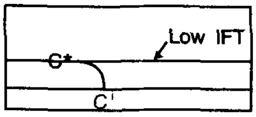
Based on these results, a logical question one might ask is why detergency levels do not drop off at temperatures greater than the PIT. For example, as shown in Figure 10,

$C_{12}E_7$ removes 3:1 cetane/oleyl alcohol soil very effectively between 20 and 60°C, although ultralow interfacial tensions would be expected only below 20°C. A likely explanation is that despite an initial excess of alcohol being present in the soil at temperatures greater than the PIT, depletion of this polar component from the thin soil films occurs during the course of the washing cycle, thereby moving the soil composition at the soil-water interface towards the optimum nonpolar/polar ratio for that temperature. As a result, a sufficiently low interfacial tension is eventually attained at some instant during the washing process, which allows removal by emulsification of the originally entrapped soil with subsequent solubilization into surfactant micelles.

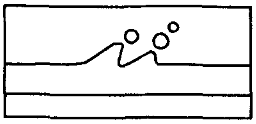
Figure 11 schematically illustrates this process. At the start of the washing cycle, the soil films have an initial uniform polar soil concentration, C^i. A changing concentration profile develops in the soil as polar components are depleted at the soil-water interface. At time, t^*, a critical concentration, C^*, is attained at the interface which yields a sufficiently low interfacial tension for emulsification of soil to occur. The removal of soil held in the smallest interfiber capillaries will require the attainment of very low interfacial tensions. As a result, C^* in that situation would necessarily match the concentration exhibiting a PIT at the wash temperature.



a) Washing Time = 0 min;
C^i = Initial Polar Soil Concentration



b) Washing Time = t^*; $C^* < C^i$



c) Washing Time > t^*; Emulsification Occurs

FIG. 11. Emulsification resulting from polar soil depletion.

Preferential solubilization of cetane into an alcohol ethoxylate solution from mixtures of cetane and triolein has been observed previously (23). For the systems of interest here, the likelihood of unequal solubilization rates is even greater since the polar soil acts as a cosurfactant and resides in the outer surfactant film of the micelle, while the nonpolar portion is solubilized into the interior of the micelle. As mentioned previously, the detergency studies using independently-labelled cetane and oleic acid show the preferential removal of the polar component required for this type of mechanism to be operative.

Evidence of changes in soil composition allowing expanded regions of optimum detergency is also found in the solubilization results shown in Figure 6. In those studies, the fastest solubilization occurred for the soil compositions exhibiting a PIT of 55°C. However, faster solubilization was found to occur if more than the optimum amount of alcohol or acid was present rather than if too little was present. In the former case, the composition of the emulsified droplets moved toward the optimum composition as polar material was depleted, thereby continually lowering the IFT and enhancing dispersion of the soil. In contrast, the systems initially deficient in alcohol or acid moved even further away from the optimum composition with time, causing the IFT to rise and inhibiting the formation of very small drops which are solubilized rapidly.

The proposal that removal of nonpolar/polar soil mixtures is influenced by interfacial tension reduction at the soil/water interface is supported by previous observations of snap-off of oil drops (Fig. 1a) rather than complete roll-up of soil in which wetting phenomena dominate (Fig. 1b) (14,15). Similar events were observed for the systems in this study. For example, Figure 12 contains a sequence of photographs showing the removal of 3:1 cetane/oleic acid from a bundle of polyester fibers by 0.05% $C_{12}E_7$ solution.

No preferential wetting of fibers by the surfactant solution was observed. Instead, very long filaments of soil streamed away from the fibers, indicating the attainment of a very low soil-surfactant solution interfacial tension only a few minutes after introduction of the surfactant. Not surprisingly, very high soil removal levels were obtained with this surfactant-soil system in the detergency studies performed at 25°C. Although not observed in these studies, formation of an intermediate microemulsion phase at the soil-water interface in an actual detergency process carried out near the PIT cannot be ruled out, especially in regions of fabric where agitation is not sufficient to disturb the soil surface.

The drop-off in detergency consistently found above the cloud point temperature is not clearly understood but probably results from the interaction of surfactant-rich phases, which separate from the water above the cloud point, and the polar components which diffuse out of the soil. Also not determined in this study is the possible role played by liquid crystal formation at the soil-water interface, a phenomenon previously observed in similar systems. A liquid crystalline phase has been observed to form around mineral oil drops containing 25% oleyl alcohol when they are contacted with a 1.5% wt nonionic surfactant solution (16). Others have observed liquid crystal formation around emulsified paraffin drops containing various quantities of fatty alcohols (24). Further phase behavior studies are needed to fully understand these phenomena.

Relationship of the PIT to the rate of soil removal. The previous discussion has been concerned with soil removal levels attained after a typical washing time, i.e., 10 min. However, if the above mechanism for removal of liquid nonpolar/polar soil blends is correct, a significant time effect should be evident when washing soils of different compositions at the same conditions. In particular, those initial soil compositions having a PIT close to the washing temperature should be removed most quickly.

The results of a detergency study examining the kinetics of soil removal are shown in Figure 13. For $C_{12}E_7$ at 50°C, very fast removal of the 9:1 cetane/oleyl alcohol soil was found. This behavior can be attributed to that composition having a PIT close to 50°C, as shown in Figure 2. The soils containing larger quantities of oleyl alcohol were initially removed more slowly since they had much lower PITs. However, their removal increased steadily with time as the soil composition at the water interface approached the opti-

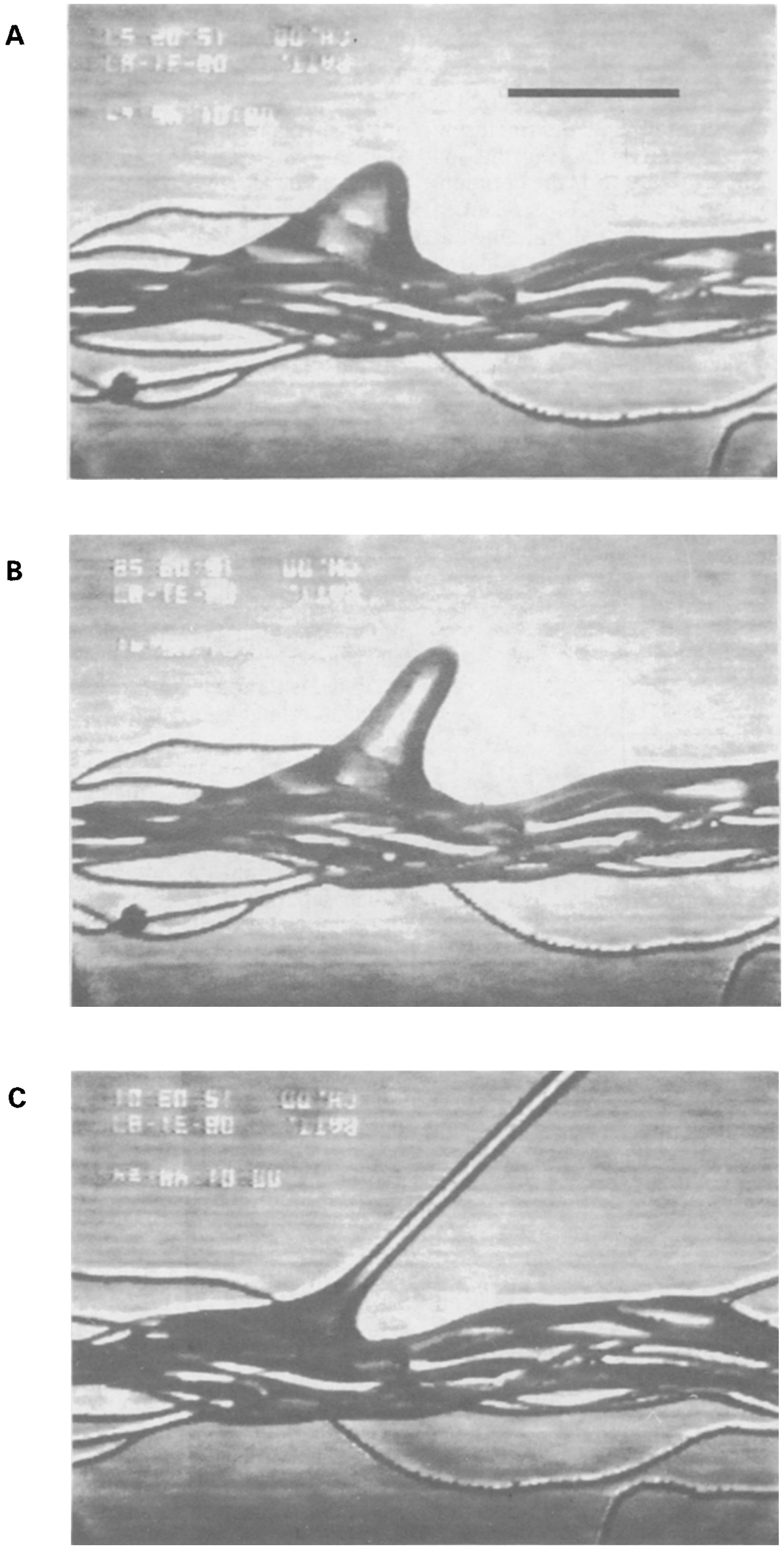


FIG. 12. Removal of 3:1 cetane/oleic acid from polyester fiber bundle. Detergent, 0.05% $C_{12}E_7$; temperature, 25°C; scale, bar = 0.3mm; elapsed time, a) 105 seconds, b) 106 seconds, c) 109 seconds.

mum for 50°C (slightly less than 10% oleyl alcohol). In contrast, the removal of the cetane-only soil leveled out quickly at a lower value, since the PIT for the $C_{12}E_7$/water/cetane system is about 85°C. As a result, a low IFT was not attainable at any time with that system. This kinetic study points out that PIT-composition plots, like those in Figures 2 and 3, are useful for predicting at what temperature the fastest removal of a soil will occur.

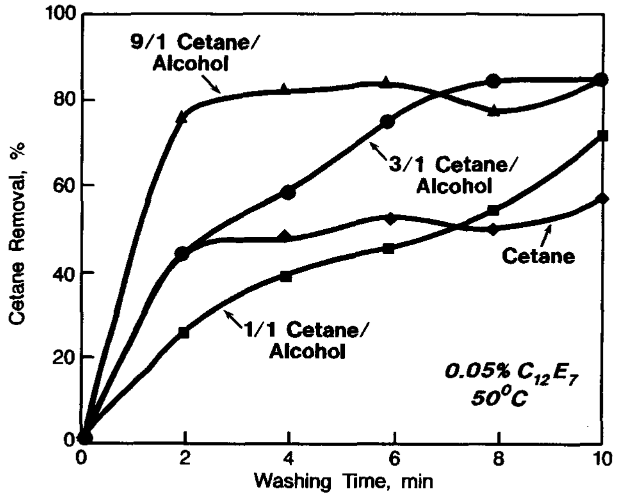


FIG. 13. Kinetics of cetane removal from cetane/oleyl alcohol blends.

Relevance to previous studies. As shown in Figures 2 and 3, the presence of long-chain fatty acids and alcohols has a dramatic influence on the phase inversion temperature of hydrocarbon/water/alcohol ethoxylate systems. Specifically, less than 5% long-chain acid or alcohol in cetane is sufficient to lower the PIT and optimum detergency temperatures to below the cloud point of the surfactant solution. This situation in which polar materials present in a liquid soil reduce optimum washing temperatures is related to the case in which water-insoluble alcohols or low-HLB surfactants are added in small amounts to aqueous solutions of alcohol ethoxylates to enhance low-temperature removal of nonpolar soils (3,5,25). In the latter case, the additive acts with the surfactant to form a mixed surface-active film which lowers the effective PIT of the system (5). However, being initially present in the aqueous solution, the alcohol or low-HLB surfactant also reduces the cloud point. Therefore, the PIT remains above the cloud point in those systems. Also, since an excess amount of polar additive is not present in the soil, the soil composition remains essentially fixed, and optimum detergency occurs only at the PIT.

To simplify the interpretation of the detergency mechanisms, several detergency variables were not considered in this study. For example, the influence of alkalinity and water hardness on the removal of soils containing fatty acids is quite pronounced. In this regard, the effects of triethanolamine and water hardness have been studied by others with relation to the removal of mineral oil/oleic acid soils from polyester film by solutions of commercial nonionic surfactants (14). In the absence of electrolyte, the removal of a 5% oleic acid soil was inhibited by the presence of triethanolamine. However, the addition of water hardness was found to reverse this effect and promote emulsification. These trends were attributed to changes in the soil-water interfacial tension resulting from different counterions being associated with the oleate ions. An interesting future study would be to determine whether the phase behavior and solubilization techniques used in this work would be applicable to systems in which *in situ* neutralization of acid soils occurs.

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